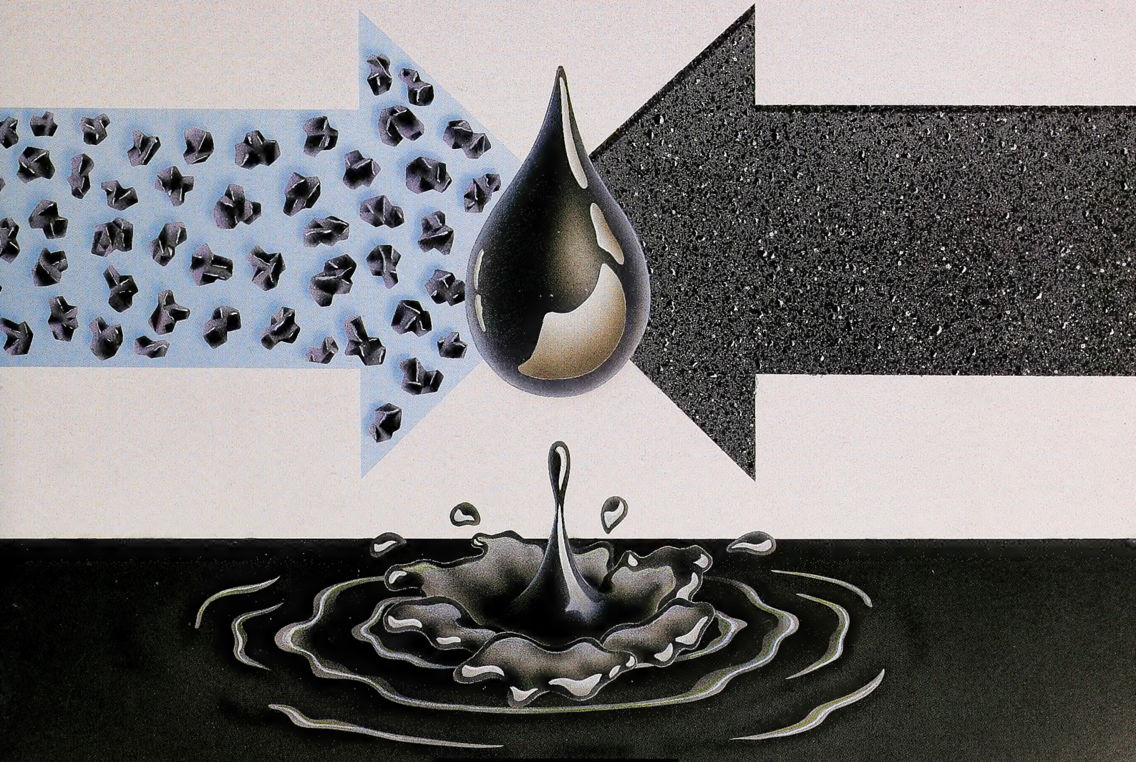
Alberta ENERGY

Scientific and Engineering Services

Co-processing Studies of Alberta Subbituminous Coals

Projects supported in part by the Alberta/Canada Energy Resources Research Fund



ALBERTA OFFICE OF COAL RESEARCH & TECHNOLOGY

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Foreword

Since 1976, numerous projects have been initiated in Alberta by industry and by academic research institutions which are aimed at better utilization of Alberta's energy resources.

These research, development and demonstration efforts were funded by the Alberta/Canada Energy Resources Research Fund (A/CERRF), which was established as a result of the 1974 agreement on oil prices between the federal government and the producing provinces.

Responsibility for applying and administering the fund rests with the A/CERRF Committee, made up of senior Alberta and federal government officials.

A/CERRF program priorities have focused on coal and conventional energy resources, as well as energy conservation and renewable energy. Program administration is provided by staff within the Scientific and Engineering Services and Research Division of Alberta Energy.

In recognition of the importance of coal to Alberta's economy, the Alberta Office of Coal Research and Technology was established in 1984 within Alberta Energy and Natural Resources (now Alberta Energy). Its primary purpose is to encourage the development and application of new technologies related to Alberta coals. The Office provides funding contributions to research and development projects in industry, academic institutions and other research establishments and monitors their progress in an overall program of improving the production, transportation and marketability of Alberta coals.

In order to make research results available to industry and others who can use the information, highlights of studies are reported in a series of technology transfer booklets. For more information about other publications in the series, please refer to page 14.

Co-processing Studies of Alberta Subbituminous Coals

Conventional crude oil production from established Canadian oil fields is expected to decline sharply after 1990, although the precise timing will depend on such factors as energy demand and price, the use of enhanced oil recovery methods and the extent to which new discoveries can be added to current reserves.

When production begins to wane, any shortfall between domestic consumption of petroleum products and the ability of conventional sources to supply crude oil must be made up by crude oils from frontier areas, imports and increased production of synthetic crude oils. Some or all of these may not be equivalent to the light crude oils currently supplied to Canadian refineries.

The bitumen in Alberta's oil sands deposits is already an established source of synthetic crude oils, and the heavy oils found elsewhere in Alberta and Saskatchewan will become a second source of refinery feedstocks after upgrading facilities are built. A third source could be Alberta's vast deposits of subbituminous coals.

While production of synthetic crude oils from coal or bitumen can be entirely separate operations, research work, financed in part by the Alberta/Canada Energy Resources Research Fund (A/CERRF), indicates that a more promising alternative is to produce liquid fuels from mixtures of coal and bitumen. This is called "co-processing," and it has been the subject of several research investigations in Alberta since 1979.

Initial Laboratory Investigations at Alberta Research Council

Processes to generate liquid petroleum products from coal are being developed in several countries using European, American, Japanese or Australian coals, which differ from western Canadian coals in several important ways, including physical and chemical characteristics and geological setting.

Consequently, in 1979 a coal liquefaction program was launched at the Alberta Research Council to investigate the suitability of using Alberta coals in a variety of existing coal liquefaction processes. In particular, this effort focused on subbituminous coal because it is the most abundant coal rank found in Alberta.

Subbituminous coals from nine deposits representing the Paskapoo and Horseshoe Canyon formations of Alberta were tested under conditions that were typical of five liquefaction processes. At the time, all these processes were at some stage of development in Japan, the United States and the Federal Republic of Germany.

More than 100 "scoping" experiments were carried out in 35-ml or one-litre autoclaves to (1) obtain data that would enable relative ranking of individual coals, (2) indicate those process conditions best suited to different coal regions, and (3) identify promising processes for detailed evaluations in semi-continuous and continuous-flow bench

Mean Conversion Values and Standard Deviations (%) in Liquefaction Studies of Alberta Subbituminous Coals

Group of Coals	No. of Coals	Solvent: Anthracene Oil			Solvent: Bitumen	
		PC-1* Mean Conversion	PC-2* Mean Conversion	PC-3* Mean Conversion	PC-4-1* Mean Conversion	PC-4-2* Mean Conversion
Paskapoo	4	71±9 (9)**	84±5 (11)	86±4 (14)	79±4 (8)	84±2 (9)
Horseshoe Canyon	4	90±3 (8)	95±1 (11)	96±1 (8)	94±2 (10)	95±1 (10)

* represents individual liquefaction processes

** figures in brackets represent number of experiments

(Source: *Autoclave Liquefaction Studies of Alberta Subbituminous Coals*, Alberta Research Council, March 1985)

reactors. Those process variables that were studied included the following: catalyst type and concentration; the use of coal-derived solvent (anthracene oil), bitumen and bitumen-derived solvents; hydrogen gas; carbon monoxide and steam mixtures; heating rate; reaction time; and temperature.

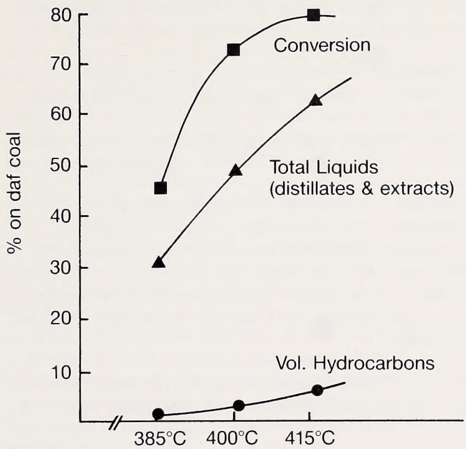
The liquefaction processes were of two types: (1) solvolytic, in which coal and solvent are heated at 400°C in an atmosphere of carbon monoxide and steam; and (2) hydrogenation, in which coal and solvent are reacted with hydrogen in the presence of a catalyst at temperatures ranging from 400°C to 470°C.

From the results of these screening experiments, it was learned that the conversion of subbituminous coal under most conditions ranged from 81 to 94 per cent. Coals from the Horseshoe Canyon Formation were found to be more reactive than those from the Paskapoo Formation over the entire range of liquefaction conditions. Of particular significance was the discovery that the use of bitumen as a solvent resulted in conversion rates that were comparable to those obtained when anthracene oil was used, even though the reaction conditions that were used with bitumen were less severe than for anthracene oil. This was the first indication that once-through co-processing with bitumen might have some advantages over conventional liquefaction processes that require a recycle stream of process-derived oil, of which anthracene oil was representative.

While these screening experiments were under way, some studies were begun using high volatile bituminous coal with oil sands bitumen, heavy oils, or liquid derivatives from bitumen as solvents under catalytic hydrogenation conditions. The results of these experiments further emphasized the value of co-processing coal with either bitumen or heavy oil.

Using reaction conditions similar to those in the bituminous coal experiments, additional autoclave studies were conducted with six types of subbituminous coals representing the range of geographic, rank and geological variations found in Alberta. Also, comparisons were made between catalytic hydrogenation and carbon monoxide/steam reducing systems. Other experiments were carried out using anthracene oil as a solvent to compare co-processing results with more conventional liquefaction systems.

Effect of Temperature on Per Cent Coal Conversions and Product Distribution from Co-processing Ardley Coal and Suncor Bitumen



(Source: *Co-processing of Alberta Subbituminous coal with oil sand Bitumen*, Moschopedis, S.E. and B. Ozum. Liquid Fuels Technology, 2(2), 193-209 (1984))

Coal solubilization (the process of converting coal from solid to liquid phase) was accomplished using reducing agents such as hydrogen and carbon monoxide. At temperatures below 400°C, the rate of conversion of coal to pyridine-soluble products was considerably faster than when carbon monoxide was the reducing agent. The products of carbon monoxide/steam treatment were viscous; approximately half the product was solid at room temperature. It would require further upgrading.

From 1983 to 1985, numerous experiments were carried out to refine the process conditions and prepare for experiments in two-stage reactors.

Much of this process refinement involved subbituminous coal from the Highvale Mine, which was one of the less reactive coals from the Paskapoo Formation. Process variables that were studied in autoclaves included comparisons between carbon monoxide/steam and catalytic hydrogenation, a variety of catalysts, temperatures ranging from 370°C to 410°C and variable residence time.

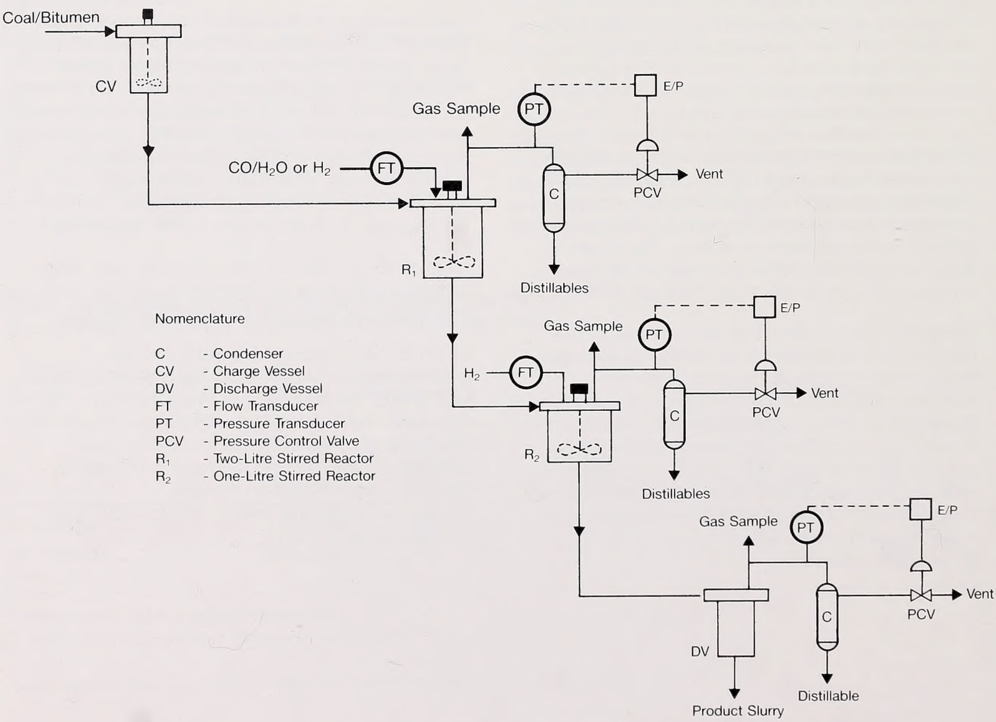
For the first time in this experimental program, co-processing was carried out in a semi-continuous, two-stage, bench-scale Hot Discharge Unit (HDU) that used a two-litre stirred autoclave in the first stage and a one-litre stirred autoclave in the second stage. During 1984/85, approximately 30 experiments were completed using the HDU.

The results were analysed in terms of coal conversion, distillable oil yield and product quality. It was found that carbon monoxide/steam was more effective than catalytic hydrogenation for first-stage solvolysis at 370°C and 390°C, and there was no advantage in using higher temperatures. The most effective combination of reducing gases and catalysts in the two-stage system was carbon monoxide/steam and potassium carbonate in the first stage, and hydrogen plus potassium molybdate in the second stage. This resulted in conversions exceeding 90 per cent with a 66 per cent distillable oil yield.

When a feedstock comprising 70 per cent bitumen and 30 per cent Highvale coal (daf basis) was co-processed in the HDU, it produced distillable oil yields equal to those from the hydroprocessing of bitumen alone. Measurements of the quality of the products from each of the process stages showed that the coal contributed little to the distillable fraction in the low-severity solvolysis stage; conversion of coal to distillable oil occurred primarily in the second stage. The precise contribution of coal to the distillable oil fraction, however, could not be determined.

In addition to the low-severity carbon monoxide/steam solvolysis experiments, the co-processing behaviour of Alberta subbituminous coal and bitumen was investigated under mild hydrogenation conditions. These tests used a 2 kg/h two-stage, continuous-flow, stirred-tank reactor. Representative coals from the Paskapoo (Highvale) and Horseshoe Canyon (Vesta) formations were processed with topped bitumen from the Athabasca and Cold Lake deposits, over a temperature range of 400-470°C and under hydrogen pressure of 14-21 MPa.

Hot Charge/Discharge Unit



(Source: *Studies on Co-processing Highvale Coal and Bitumen*, G. Kovacik in *ENR-ARC Coal Conversion Research Program — Final Reports for 1984/85, Volume 1*, Alberta Research Council, December 1985)

Results obtained from these experiments support the findings of the scoping study: coals from the Horseshoe Canyon Formation are more readily converted to liquid fuels than coals from the Paskapoo Formation. When a feedstock comprising 35 weight per cent (daf basis) Vesta coal and 65 weight per cent Cold Lake atmospheric distillation bottoms was processed in the continuous-flow stirred-tank reactor using low-cost iron oxide catalyst, distillable oil yield was 63 weight per cent (daf coal plus bitumen basis) of the feed.

The resulting synthetic crude oil has a high nitrogen and sulphur content. For example, the sulphur content of the light oil, medium/heavy oil and residual oil fractions was 1 to 2 per cent, 2 to 3 per cent and 2.5 to 3.5 per cent, respectively. Although a general decrease in sulphur content with increasing severity was observed, further hydro-treating is required to reduce the nitrogen and sulphur levels so as to satisfy refinery feedstock specifications.

Feasibility Study

HRI Inc. Analysis

While laboratory investigations were under way at the Alberta Research Council, co-processing methods being developed elsewhere were showing interesting results. Also, processes for the production of synthetic crude oil from heavy crudes were evolving into commercial-scale operations. Consequently, HRI Inc. of New Jersey undertook a feasibility study to assess several process options for producing synthetic crude oil. Various proportions of coal in the feedstock and/or as a fuel were used to produce steam required in the process.

Seven options for the commercial production of synthetic crude oil were examined. They involved three proprietary processes: H-Oil, COIL and H-Coal. The evaluation considered Lloydminster heavy crude oil and subbituminous coal from Alberta's Egg Lake Mine as the feedstock components. It was also assumed that hydrogen, required in all the processes, would be derived from natural gas.

For the particular process assumptions used in this study, it was found that the yield of synthetic crude oil per barrel of heavy crude oil feedstock increased directly with the use of coal. For example, when coal was absent from the feedstock in the H-Oil process, the yield was 0.63 barrel of synthetic crude oil for each barrel of heavy crude oil; however, direct co-processing of coal and heavy oil in the COIL process was expected to increase the yield of synthetic crude oil to 1.13 to 1.19 barrels for each barrel of heavy oil.

When the overall costs of producing synthetic crude oil were considered, it was found that production by direct liquefaction of heavy oil or coal alone was more expensive than any of the coal-as-fuel or co-processing options. It was concluded that using coal and/or natural gas as a fuel was attractive. Also, the option of using coal as a component of the co-processing feedstock was promising. When used in co-processing, coal offered the additional advantage of greater feedstock flexibility.

Coal/Heavy Oil Hydrogenation Plant Feasibility Study

The HRI study was followed in 1985 by an evaluation of the Saarbergwerke AG coal liquefaction process, developed by Gesellschaft für Kohleverflüssigung mbH (GfK) in the Federal Republic of Germany, with modifications based on the experimental work that had been conducted at the Alberta Research Council. Unlike earlier feasibility studies of coal conversion, which assumed the production of a synthetic crude oil, this particular analysis considered a process for the production of high-value transportation fuels from low-cost feedstocks.

The study, which was jointly funded by Contar Systems Engineering Ltd., Canadian Utilities Limited, GfK, Luscar Ltd. and A/CERRF (via the Alberta Office of Coal Research and Technology), was carried out by Kilborn Kellogg Rust Ltd. (now Kilborn Energy Inc.). It incorporated the following elements:

(1) fractionation and hydrogenation of Lloydminster heavy oil feedstock to produce naphtha, middle distillate fractions and a hydrogenated residuum stream;

(2) oil agglomeration of run-of-mine subbituminous coal to yield a low-ash coal feedstock;

(3) two-stage hydrogenation of agglomerated coal and hydrogenated heavy oil residuum, using carbon monoxide and steam in the first stage and hydrogen in the second stage (based on Alberta Research Council studies);

(4) de-ashing of coal/heavy oil hydrogenation residue to recover distillable oil;

(5) hydro-treating the naphtha and middle distillate streams derived from heavy oil and coal/heavy oil residuum to produce distillate fuel;

(6) catalytic reforming of hydro-treated naphtha to produce a gasoline blend stock; and

(7) production of hydrogen and carbon monoxide by the steam reforming of natural gas.

While it was acknowledged that several steps of the proposed process were not proven on a commercial scale, the evaluation was made on the basis of a plant that could handle the following: approximately 3 800 tonnes a day of run-of-mine subbituminous coal, 4 800 m^3 a day of undiluted heavy oil and 1.1 million m^3 a day of natural gas.

From the technical and economic analysis of this proposed co-processing scheme, it was concluded that co-processing of coal and heavy oil could result in liquid yields that are equal to, or greater than, those from the separate processing of coal and heavy oil. This was believed to be caused by the ability of heavy oil residuum to donate hydrogen to the coal.

By using carbon monoxide and steam in the first stage, a substantial amount of the oxygen that is present in coal can be easily removed in the process, thus allowing more efficient use of hydrogen in the second stage.

It was also concluded that the economics of producing transportation fuels by co-processing heavy oil and subbituminous coal are favourable, and that a coal/heavy oil hydrogenation process should be developed in Alberta with the objective of building a commercial-scale plant in the mid-1990s. It was emphasized that Alberta is a unique location for this operation because substantial reserves of low-cost coal, heavy oil and natural gas are readily available.

The PYROSOL Process

Following the Kilborn study, GfK devised a low severity approach to coal liquefaction. This led to a licensing agreement between Contar Systems Engineering Ltd. and GfK, allowing Contar (now known as Canadian Energy Developments Inc.) to use this patented process known as PYROSOL.

While details about the PYROSOL process are confidential, when compared with the combination GfK/Alberta Research Council process (now known as the CCLC Process) examined in the Kilborn study, PYROSOL is said to use less severe operating conditions while producing similar yields of light distillate products. Furthermore, it is claimed that the capital costs of PYROSOL are substantially lower than for the CCLC Process.

At the time the licensing agreement was signed, all of GfK's PYROSOL tests had been done in the Federal Republic of Germany and were aimed at direct liquefaction of bituminous coal from the Saar region. On the other hand, the Edmonton-based Canadian Energy Developments Inc. (CED) proposed to develop the process for co-processing heavy oil and subbituminous coal. The Alberta Research Council was contracted by CED to simulate the process on a laboratory scale using Battle River subbituminous coal and Cold Lake heavy oil. These laboratory investigations confirmed the viability of PYROSOL using Alberta feedstocks.

Subsequently, in 1986 a four-year process development program was initiated to test both the PYROSOL and CCLC processes in a continuous bench-scale unit and an automated pilot-scale unit. Since then, experiments have also begun at GfK in a six-tonne-a-day pilot plant. Results from the pilot plant work will be made available to CED. This development program is still in progress.

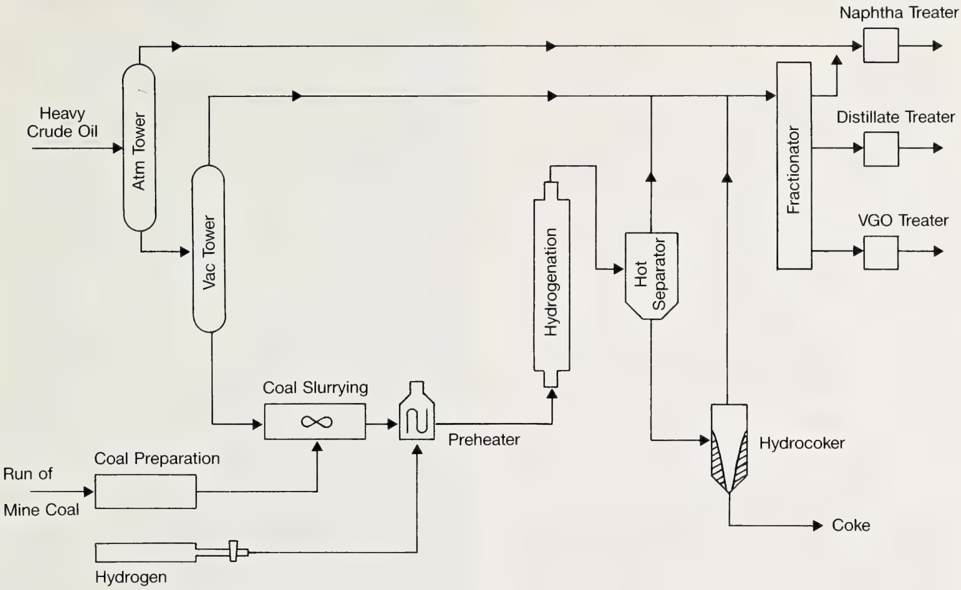
Co-processing Improvements

To further enhance the relative economic position of co-processing versus liquefaction of bitumen or heavy oil, a review was made at the Alberta Research Council of the most current liquefaction process schemes that relate to heavy crude upgrading or direct coal liquefaction, including "low severity" processes.

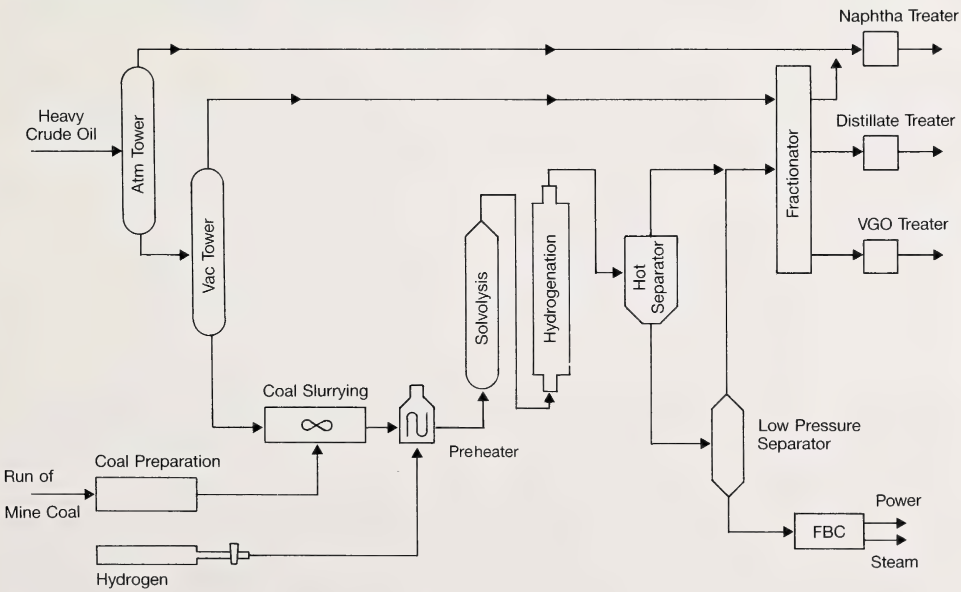
From this analysis, several recommendations were made for areas of investigation that might lead to better economics for PYROSOL, which is regarded as the state-of-the-art, low-severity method of co-processing coal and heavy oil.

These suggestions form part of the ongoing process development work being conducted by Canadian Energy Developments Inc.

Pyrosol Process



CCLC Process



(Source: Canadian Energy Developments Inc.)

Evaluation of Co-processing Schemes

Coal liquefaction plants are relatively complex hydrocarbon refineries which normally include solids handling and disposal systems, large-scale hydrogen production units, and product gas and wastewater clean-up facilities. Because few such plants have ever been built on a commercial scale, it is difficult to assess the economic viability of various liquefaction processes. Therefore, it was decided that a simple evaluation technique should be developed to provide relative process economics and identify promising options.

In this study conducted at the Alberta Research Council, an economic evaluation strategy was chosen. It consisted of establishing a hypothetical "base case" multi-stage liquefaction process that co-processes coal and bitumen under moderately severe conditions without a recycle stream.

The hypothetical, multi-stage co-processing scheme employed thermal hydrogenation in the presence of a disposable iron catalyst in the first stage. This was followed by catalytic hydrogenation using a highly active supported nickel/molybdenum catalyst in an ebullated bed reactor. In the third and final stage, conventional delayed coking was used to recover the maximum amount of distillable oil and provide a solid residue that can easily be handled and used as a fuel. Supporting this central component of the process were coal agglomeration, heavy oil fractionation, acid gas removal, hydrogen production, product upgrading, light ends recovery and various offsite facilities and utilities. The plant size was based on 100 000 kg/h of coal (daf basis), combined with 35 700 barrels a day of heavy oil.

Using experimental data from studies of Battle River coal and Cold Lake heavy oil, the overall mass balance for the hypothetical process produced an estimated yield of approximately 69 per cent of distillable oil when a coal concentration of 35 per cent was used.

Capital and operating costs were calculated and then a discounted cash flow analysis, return-on-equity business simulation model was used to generate financial information.

A more severe hydrogenation process and the PYROSOL co-processing scheme were then subjected to the same analysis.

To provide a relative ranking of the three processes, a "Figure of Merit" evaluation model was developed which assigned a score from 0 to 100 for yield, product potential, process severity and process complexity. The most attractive process was the one with the highest total score.

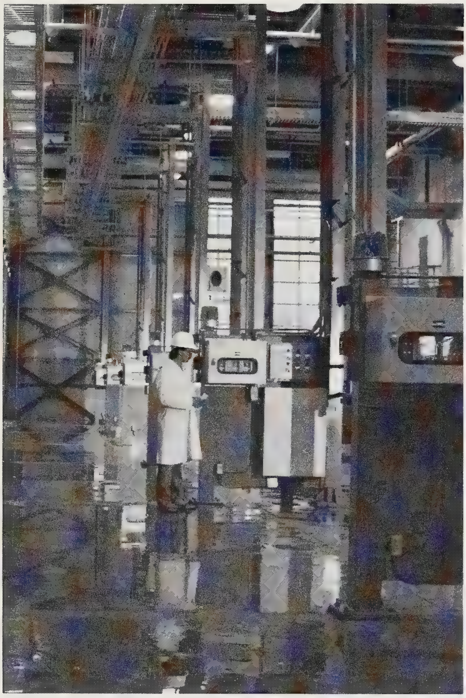
The evaluation indicated that PYROSOL was the most favourable, followed by the multi-stage process and severe hydrogenation, in that order. To validate the Figure of Merit model, a traditional discounted cash flow analysis was performed. It showed the same trends.

Process Refinements

Those elements of any coal liquefaction process, including co-processing, that have the greatest effect on process economics are temperature, pressure and reactor residence time. It follows, therefore, that significant changes to any of these factors can have a measurable, and perhaps sizeable, effect on the capital and operating costs of a commercial-scale coal liquefaction plant.

Although it appears that the PYROSOL process has some important cost and product advantages over competing co-processing systems, and it uses operating conditions that are less severe than other processes, it was decided in 1986 to explore methods of further reducing the process severity.

Term	Weighting	Multi-stage	PYROSOL	Severe Hydrogenation
Yield	1.0	54.6	63.2	57.2
Product Potential	1.0	72.2	81.0	81.0
Low Severity	1.0	55.1	52.5	29.6
Simplicity	1.0	86.2	88.6	88.7
Figure of Merit		267.4	285.3	255.5
DCF ROE		26.6%	28.7%	19.9%



Alberta Research Council studies of coal/bitumen co-processing are carried out in the High Head Laboratory of the Coal Research Centre, Devon.
(Photo courtesy of Alberta Research Council)

Coal Chemistry

To be successful, a coal liquefaction process must be capable of producing products that are desired. In the case of Alberta, a synthetic crude similar to that made from bitumen is normally assumed to be the minimum standard that must be met. It has a hydrogen-to-carbon ratio of 1.8 to 1.9. To produce this synthetic crude from bitumen, which has a hydrogen-to-carbon ratio of 1.5, hydrogen must be added at some stage of the conversion process. Alberta's subbituminous coals are even more hydrogen deficient; their hydrogen-to-carbon ratios are only 0.7 to 0.9. Therefore, even greater amounts of hydrogen must be added when coal is liquefied by itself. This requirement, however, can be reduced somewhat by co-processing with bitumen.

Most hydrogen-addition processes take place at temperatures in excess of 400°C because, it is believed, hydrogen does not react appreciably with coal at lower temperatures. Furthermore, for liquefaction to occur, carbon-carbon bonds in the coal structure must be ruptured. To do this, energy in the form of heat must be supplied to the system, usually at temperatures above 350°C. Hence, most coal liquefaction processes are carried out at high temperatures.

Similarly, experience has shown that high pressure and extended residence time produce higher rates of conversion of coal to liquid products. They also increase the distillable oil portion of the product mixture. Consequently, most coal liquefaction processes operate (1) at temperatures between 420°C and 470°C, (2) at pressures between 17.2 and 20.7 MPa (2 500 - 3 000 psi), and (3) have residence times of one to two hours. However, theoretical calculations have shown that a significant reduction in any of these conditions would represent a less severe technology. The result would be lower process costs, making coal liquefaction more competitive with synthetic crude production from heavy oil or bitumen.

The point at which hydrogen is added to a liquefaction process will influence the nature of the final products. It is generally believed that hydrogen should be present when the carbon-carbon bonds of coal are broken and the coal is solubilized. This is because hydrogen stabilizes the newly formed coal fragments and helps minimize their tendency to repolymerize.

From this perspective, a review was made at the Alberta Research Council of 13 processes that represent recent advancements in hydrogen addition under conditions that are less severe than those commonly used to liquefy coal.

Four approaches were selected for study: coal solubilization (the process of converting coal from the solid phase to the liquid phase) with supersolvents; coal solubilization with hydrogen-enhanced bitumen; hydrogen/hydrogen sulphide reducing gas systems; and coal solubilization by alkylation methods.

A supersolvent, N-methylpyrollidone, successfully solubilized up to 72 weight per cent of the coal at 350°C and ambient pressure, but solvent decomposition and recovery were identified as major obstacles in developing a process.

Hydrogen-enhanced bitumen was produced by catalytic hydrogenation and then used as a solvent for coal. High coal conversions to good quality liquid product were achieved at approximately 400°C and 6.9 MPa hydrogen pressure. Although these conditions are more severe than those used in the supersolvent work, the pressure is well below the 14-21 MPa of conventional processes.

Alkylation techniques at mild severity were unsuccessful. They achieved a maximum coal conversion of only 27 weight per cent.

Two ionic hydrosulphide additives were evaluated for improving coal solubilization. However, no substantial improvements in coal conversion or product distribution were found. The hydrogen-donor program was discontinued.

Meanwhile, investigations by Dr. N. Berkowitz at the University of Alberta revealed that with some Alberta coals, conversion reactions initiated at 400°C continued while the reaction mixture was allowed to cool. This raises questions about the current views regarding liquefaction mechanisms and is the subject of ongoing investigations.

Characterization of Coal Liquids

The chemical changes that occur when coal is liquefied, or bitumen is upgraded, are complex enough, but when the two processes occur simultaneously, as they do in co-processing, understanding the chain of events that ultimately leads to products becomes even more difficult.

Consequently, a project was initiated at the Alberta Research Council with the objective of gaining a better understanding of the interactions between coal and bitumen. Primarily, the project will provide chemical and physical characterizations of the co-processing feedstock and products and will include a performance characterization of the latter.

This work entails the following:

1. separation of high molecular weight and low molecular weight components;
2. separation of resins from oils;
3. separation of hydrocarbons into saturates and several aromatic fractions;
4. separation of asphaltenes by size;
5. the use of field-ionization mass spectrometry;
6. thermogravimetric analysis;
7. evaluation of structural groupings in asphaltenes by nuclear magnetic resonance;
8. routine analyses as required; and
9. determination of the octane and cetane ratings of the reaction products.

It is anticipated that the outcome of this investigation will also help identify those components of synthetic crude oils that are responsible for catalyst poisoning in various hydro-treating and refining processes.

The project is continuing.

Isotopic Mass Balance

The mixture of products resulting from co-processing and the process economics are influenced by the proportions of coal and bitumen used in the feedstock.

Therefore, knowing how much each feedstock component contributes to the chemical composition of the products is important, as it could be the basis for a useful process control method.

The first analytical technique capable of distinguishing between the contributions made by coal and bitumen to the co-processing products was developed in a joint project involving the Alberta Research Council and the University of Alberta. This technique, called isotope mass balance, measures the abundance ratio of the carbon-13 isotope to the carbon-12 isotope in carbon-containing substances.

When the $^{13}C/^{12}C$ ratios of bitumen and Alberta subbituminous coals were measured by this technique, it was found they differed significantly from each other. This suggested that analysis of co-processing products should reveal how much carbon was contributed by each of the feedstock components.

Therefore, the feedstocks and products of typical co-processing experiments at the Alberta Research Council were converted to carbon dioxide at high temperature, and the $^{13}C/^{12}C$ ratio was measured by mass spectrometry.

Under conditions employing the addition of hydrogen or carbon monoxide/steam in single-stage autoclaves, and using Highvale coal and bitumen, it was found that 14 to 23 per cent of the carbon in the resulting synthetic crude oil was derived from coal.

In 1987, under the direction of Dr. K. Muehlenbachs of the University of Alberta, researchers at the university and the Alberta Research Council began using this analytical technique to determine whether an optimum coal-to-bitumen ratio exists from the co-processing experiments currently under way.

Further Reading

Aitchison, D.A., M.P. du Plessis and S. Wong. 1985. *Technical and Economic Aspects of Coal-Heavy Oil Co-processing Concept*. 35th Canadian Chemical Engineering Conference, Calgary, Alberta, October 6-9.

Aitchison, D.A., P. Clark, B. Ignasiak and L.K. Lee. 1986. *Reaction Severity and Feedstock Pretreatment in Co-processing*. U.S. DOE Direct Liquefaction Contractors Review Meeting, Pittsburgh, Pennsylvania, October 21 and 22.

Aitchison, D.A. and G. Hagerty. 1987. *Preliminary Economic Evaluation of a Multi-stage Coal/Heavy Oil Co-processing Concept and Development of a Simple Process Evaluation Model*. Alberta Research Council. Prepared for Alberta Office of Coal Research and Technology.

Aitchison, D.A., P. Clark, T. Ohuchi, R. Hawkins and L. Logan. 1987. *New Liquefaction Processes: Screening Studies of Four Low Severity Liquefaction Concepts*. Alberta Research Council. Prepared for Alberta Office of Coal Research and Technology.

Alberta Research Council. 1985. *Autoclave Liquefaction Studies of Alberta Subbituminous Coals, Final Report*. Prepared for Alberta Office of Coal Research and Technology.

Anderson, N.E., J.W. Caldwell, F.G. Boehm and A. Liron. 1985. *The Simultaneous Conversion of Coal and Heavy Oil to Premium Transportation Fuels*. 35th Canadian Chemical Engineering Conference, Calgary, Alberta, October 6-9.

Boehm, F.G. and A. Liron. 1985. *Co-processing of Coal and Heavy Oil - A New Development for the Advancement of Coal Liquefaction*. The Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September.

Bowman, C.W. and M.P. du Plessis. 1985. *The Canadian Synthetic Fuel Industry - A Major Use of Hydrogen*. 5th World Hydrogen Energy Conference, Toronto, Ontario.

Chakrabartty, S.K. 1985. *Search for Low Severity Liquefaction Concept*. Liquid Fuels Technology. 3: 1-13.

Chakrabartty, S.K. and M.P. du Plessis. 1985. *Evaluation of Alberta Plains Coals for Pyrolysis and Liquefaction Processes*. Alberta Research Council Coal Report 85-1.

Clark, P.D., B. Ignasiak, G. Kovacik and T. Ohuchi. 1985. *Liquefaction of Alberta Subbituminous Coals in Oil Sands Bitumen with Either CO/H_2O or H_2 Reducing Gas Atmosphere*. Miami International Conference on Alternative Energy Sources, Miami, Florida, December 9-11.

Clark, P.D., D.A. Aitchison, E. Fitzpatrick, R. Hawkins and T.L.K. Lee. 1986. *The Liquefaction of Alberta Subbituminous Coals with Iron Sulphur Catalyst Systems*. Alberta Research Council. Prepared for Alberta Office of Coal Research and Technology.

Clark, P.D. 1986. *New Liquefaction Processes: A Review of Low Severity Liquefaction Concepts*. Alberta Research Council. Prepared for Alberta Office of Coal Research and Technology.

du Plessis, M.P., B. Ignasiak, T. Ohuchi, P. Clark, G. Kovacik, R. Lott, L. Lewkowicz, T. Lee and D.A. Aitchison. 1985. *Two-Stage Co-processing of Alberta's Subbituminous Coals and Bitumen.* 1985 International Conference on Coal Science, Sydney, Australia, October 28 - November 1.

du Plessis, M.P. 1984. *Coal Utilization Options for Future Energy and Feedstock Supplies*. 35th Annual Technical Meeting of Petroleum Society CIM, Calgary, Alberta.

HRI Inc. *Economic Evaluation of Coal/Oil Co-processing*. Project report available from HRI Inc., Marketing Services, P.O. Box 208, Gibbsboro, New Jersey, U.S.A. 08026. Executive Summary available from Alberta Office of Coal Research and Technology.

Ignasiak, B. 1985. *Two-Stage Co-processing of Subbituminous Coals and Bitumen or Heavy Oil.* 2nd District Five Meeting of CIM, September 11.

Kilborn, Kellogg, Rust Ltd. 1985. *Coal/Heavy Oil Hydrogenation Plant Feasibility Study*. Prepared for Contar Systems Engineering Ltd., Alberta Energy and Natural Resources, Canadian Utilities Limited, Gesellschaft für Kohleverflüssigung mbH and Luscar Ltd.

Kirchen, R.P., L. Lewkowicz, N. Shatilla, T.G. Southern and M.P. du Plessis. 1985. *Upgrading of Synthetic Crudes. I. Catalytic Hydroprocessing of Subbituminous Coal and Athabasca Bitumen Derived Distillates*. 68th Canadian Chemical Conference, Kingston, Ontario, June 2-5.

Kovacik, G. 1985. *Studies on Co-processing Highvale Coal and Bitumen*. Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for 1985/86, Volume I. Prepared for Alberta Office of Coal Research and Technology.

Kovacik, G., M. Oguztoreli and B. Ozum. 1987. *Co-processing of Alberta Subbituminous Coal and Bitumen in a Semi-Continuous Hot Charge-Discharge Unit*. Can. J. Chem. Eng. 65: 286-292.

Lee, L.K. 1985. *Co-processing of Alberta Subbituminous Coal and Bitumen (or Heavy Oil) in a Continuous Flow Bench Scale Unit*. Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for April 1 to September 30, 1985. Prepared for Alberta Office of Coal Research and Technology.

Lee, L.K. and D.A. Aitchison. 1986. *Process Improvements: A Review of Co-processing Technology*. Alberta Research Council. Prepared for Alberta Office of Coal Research and Technology.

Lee. L.K., P. Clark, E. Fitzpatrick and R. Hawkins. 1986. *The Liquefaction of Highvale Coal in Anthracene Oil Using Dispersed Molybdenum and Alumina Supported Metal Catalysts*. 10th Canadian Symposium on Catalysis, Kingston, Ontario.

Moschopedis, S.E., R.W. Hawkins and H. Wasyluk. 1983. *Batch Autoclave Tests for the Liquefaction of Alberta Subbituminous Coals: Part II. I.G. Farben and Co-processing of Coal with Oil Sands Bitumen*. Alberta Research Council. Report #YCLQ-29.

Moschopedis, S.E. 1984. *Further Investigations on the Use of Bitumen and Heavy Oils to Process Coals*. Liquid Fuels Technology. 2:177-191.

Moschopedis, S.E. and B. Ozum. 1984. *Co-processing of Alberta Subbituminous Coal with Oil Sand Bitumen*. Liquid Fuels Technology. 2:193-209.

Moschopedis, S.E. June 17, 1984. *Coal Liquefaction Process with Oil Sand Bitumen Derived Solvent*. Canadian Patent No. 1160586.

Moschopedis, S.E., R.W. Hawkins and H. Wasylyk. 1982. *Co-processing of Coal with Oil Sands Bitumen and Derivatives: Batch Autoclave Tests*. Alberta Research Council. Report #YCLQ-13.

Muehlenbachs, K., J.G. Steers, A. Hogg, T. Ohuchi and G. Beaulieu. 1988. *Natural Variations of ^{13}C Abundance in Coal and Bitumen as a Tool to Monitor Co-processing*. 195th American Chemical Society Meeting and 3rd Chemical Congress of North America, Toronto, Ontario, June 5-10.

Ohuchi, T. and D. Parker. 1985. *Studies of Co-processing Highvale Coal and Bitumen in Autoclaves*. Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for April 1 to September 30, 1985. Prepared for Alberta Office of Coal Research and Technology.

Ohuchi, T., J.G. Steer, K. Muehlenbachs and D. Carson. 1986. *Influence of Slurry Composition on Coal Solubilization as Determined by ^{13}C Mass Balance Calculations*. Proceedings 36th Canadian Chemical Engineering Conference, Sarnia, Ontario.

Ohuchi, T., J.G. Steer, K. Muehlenbachs and D. Carson. 1987. *The Influence of Iron-Based Metal Catalyst on Coal Solubilization as Determined by ^{13}C Mass Balance Calculations*. International Conference on Coal Science, Maastricht, The Netherlands, October 26-30.

Selucky, M.L. 1986. *Coal Liquid Characterization Technical Report*. Alberta Research Council. Prepared for Alberta Office of Coal Research and Technology.

Steer, J.G., K. Muehlenbachs and T. Ohuchi. 1986. *Isotopic Measurement of the Proportion of Coal Liquefied by Co-processing*. 69th Canadian Chemical Conference, Saskatoon, Saskatchewan, June 1-4.

Steer, J.G., T. Ohuchi and K. Muehlenbachs. 1986. *Quantitative Determination of the Amount of Coal Incorporated into Synthetic Oil*. Proceedings First International Rolduc Symposium on Coal Science, Rolduc, The Netherlands, April 28 - May 1.

Steer, J.G., T. Ohuchi and K. Muehlenbachs. 1987. *Efficacy of Coal-Bitumen Co-processing as Determined by Isotopic Mass Balance Calculations*. Fuel Processing Technology. 15: 429-438.

Steer, J.G., K. Muehlenbachs, T. Ohuchi, D. Carson, B. Doherty and B. Ignasiak. 1987. *Isotopic Constraints on the Efficiency of Liquefaction of Low-Ranked Coal*. 14th Biennial Lignite Symposium on the Technology and Utilization of Low-Rank Coals, Dallas, Texas, May 18-21.

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